Short Communication

Integrated polymer thin film macroporous silicon microsystems[†]

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Abstract

Polymeric thin films with porous silicon can be used to fabricate microsystems that are superior in performance. Such devices include sensors for detection of toxic gases and microbiological organisms. Quick and simple methods to detect life-threatening gases and microbial species are very essential as contamination the toxic gases, food and water with bacteria can cause a number of food- and water-borne diseases. The advantages of these polymeric/silicon microsystems are the ease of fabrication, a high sensitivity, fast response time and the most important their room temperature operation. The sensors were prepared by vacuum-depositing doped polyaniline in the form of thin films on the silicon macroporous structures. The particular doping combination in the polymer makes the sensor specific for the detection of *E. coli.* The sensitivity of the devices as the ratio of current from the sensor obtained upon exposure to microorganisms with respect to the current obained without exposure to microorganism is very high. The reponse time of the sensor is about 10 s. The macroporus silicon substrate allows to obtain a polyaniline thin film with high specific surface area and good crystallinity, as shown, respectively, by SEM and X-ray investigations. Both the high surface area and the crystallinity of the polyaniline film deposited on the macroporous silicon substrate are believed to be responsible for the excellent properties of the sensor devices. We describe the fabrication process, the morphological, structural and electrical characterization of the polymeric thin film/silicon microsensing systems.
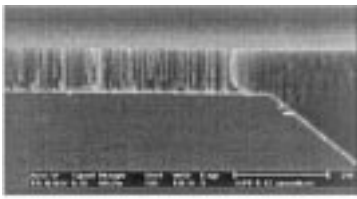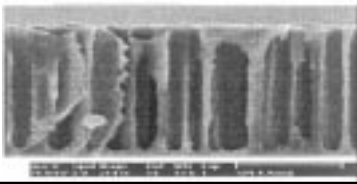
Keywords: Silicon microsystems, food- and water-borne diseases, microbial infestation, vacuum-deposited polymeric thin films, Si wafer.

1. Introduction

Food and water contaminated with bacteria can cause a number of food- and water-borne diseases. Determination of the presence of microorganisms and identification of specific causative microorganisms is necessary to control the microbial infestation. Quick and simple methods to detect the type of life-threatening microbial species are very essential. Most of the methods to detect the presence of microorganism are chemical, spectrochemical and the like, which are time-consuming and cumbersome and this eventually puts a limit on their extensive and actual use at the site monitoring. The fast detection of microbial species can be achieved by utilizing efficient response-integrated sensors. Owing to this reason, there has been an intensive effort to prepare advanced materials and structures that can be used for the preparation of fast response, room temperature-operating sensors having high selectivity and sensitivity. Our efforts have been directed to prepare sensors from vacuum-deposited polymer thin films on macroporous silicon substrates to achieve fast response, highly selective, cost-effective and room temperature-operating hybrid Si/polymer sensor for the detection of microbiological organisms.

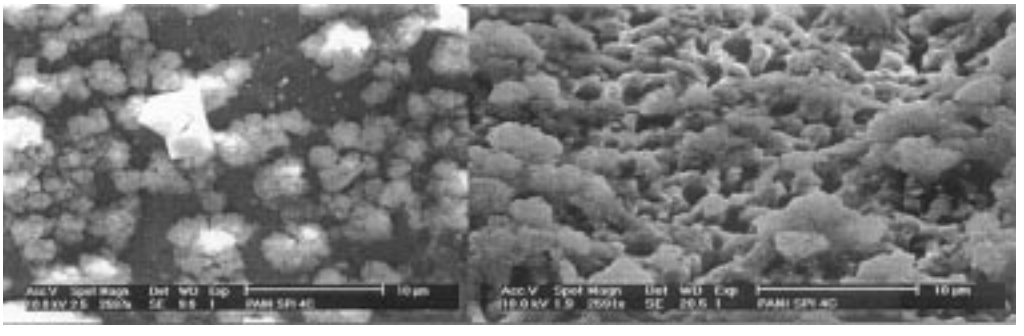| Substrate resistivity -*n* type	Samples	Example of porous morphology	Polymer deposition
2.2 Ω. cm	SPI-3 No anodization Reference sample		Polyaniline Thin film 1000 nm
0.05 Ω. cm	ST8-6A		
	SPI-3A		
2.2 Ω. cm	SPI-4C		
	SPI-4D		

FIG. 1. Scanning electron micrographs of polyaniline thin films deposited on flat and MPSS.

2. Experimental

N-type (100), 0.05 Ωcm resistivity double-side polished Si wafer has been used as a starting substrate. To realise several micron-thick Si membranes, bulk micromachining (Si etching from the back side of the wafer) with 40% in weight KOH mixture at 80°C was used. The silicon areas to be etched, on the back of the wafer, as well as the areas to be anodized, on the front of the wafer, were opened on a 200 nm LPCVD Si_3N_4 masking layer. To form a macroporous structure throughout the entire Si membrane thickness, a custom-built double electrochemical cell was used. During the anodization process, the sample was lighted on the backside using a 250W halogen lamp and a high-pass optical filter. The HF concentration, photocurrent density and anodization time were carefully tuned to obtain proper macropore size and density. After the macroporous structure formation, a thermal oxidation cycle at two different temperatures (T = 350°C in dry O_2, 850°C in wet O_2, respectively) was performed to provide the necessary dielectric insulation between the core Si in the macroporous structure and the sensing layer. The formation of macroporous silicon membrane was followed by vacuum-deposition of thin films of polyaniline prepared as follows.

First, a copolymer of aniline and formaldehyde was prepared by adding aniline monomer in dilute hydrochloric acid. To this, a formaldehyde solution was added with constant stirring. The resultant solution was allowed to stand for a specific time and then Fe was added in the form of a salt. The resultant solution was stirred for 30 min and poured into 15–20% NaOH solution. The precipitate obtained was filtered, washed with distilled water until the filtrate was free from alkali and dried in oven. The powder so obtained was used for fabrication of pellets and for preparation of polymeric films by vacuum evaporation on glass substrate. The thickness of the films was monitored and controlled by quartz film thickness monitor and was estimated to be of the order of 700 nm. The vacuum-deposited gold contacts were provided to these thin films. The sensitivity characteristics of the samples without and upon exposure to microorganisms were measured in metal/polymer/metal sandwich and lateral structure configuration. The sensitivity characteristics of the sensors were measured using a Keithley SMU236 source measure unit with a computerized interface for automation. The measuring cell was made of glass. Colonies of microorganisms having different concentrations were prepared on micro glass slides, using various culture media. This provided a range of concentration of microorganisms for evaluation. The microscopic slides containing microorganisms were placed at the bottom of the cell. The sensor was placed inside the cell in the environment comprising microorganisms in air. The determination of the concentration of the microorganisms in air in the vicinity of the sensor was carried out while preparing the microorganism colony using cultures. The morphology of macroporous silicon substrate and polyaniline/MPSS structure was studied with high-resolution scaning electron microscope and X-ray techniques.

3. Results and discussion

Figure 1 shows the fabrication process of the integrated polyaniline/MPSS-sensing device prepared by vacuum-deposition of polyaniline thin film on oxidized macroporous silicon substrate. Since the undoped polyaniline films do not respond to any microorganisms, various dopants were used to make the polyaniline film selective and specific to a particular microorganism. Figure 2 shows the schematic of the vacuum-deposited polyaniline/macroporous silicon-sensing device. Figure 3 shows the X-ray diffractogram of polyaniline films deposited on MPSS. During evapo-
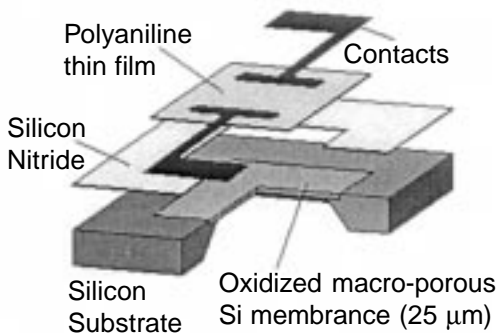
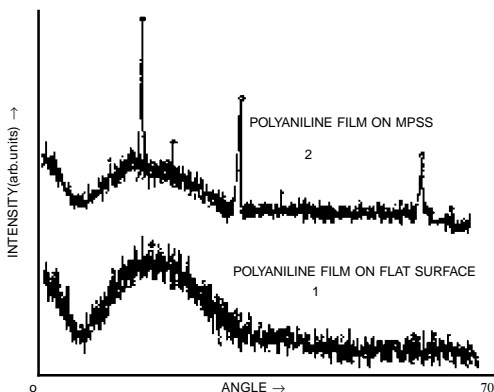FIG. 2. Schematic of vacuum-deposited polyaniline/MPSS sensor.

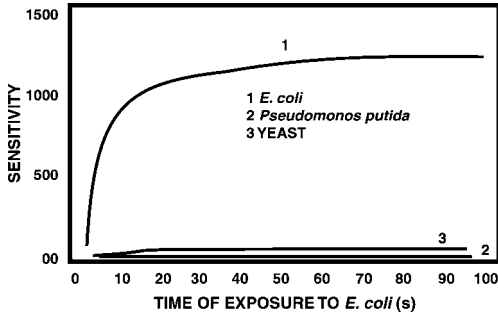FIG. 3. X-ray diffraction of polyaniline films.

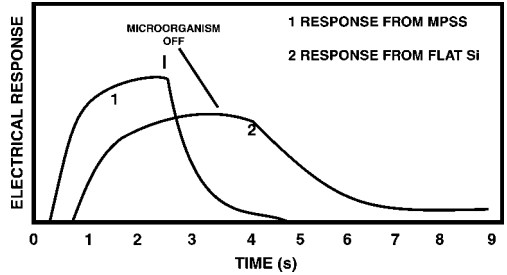FIG. 4. Sensitivity of polyaniline/MPSS sensors.

FIG. 5. Sensor response.

ration of the doped polyaniline powder the molecules and long chains are evaporated to make the film. A repolymerization of the whole takes place at the substrate. This process of evaporation–condensation repolymerization results in well-oriented thin films rich in nanocrystals of Fe-doped polyaniline complex molecules and chains. The electrostatic potential of the Fe ion in the polyaniline film is specific of the process making it sensitive only for *E. coli*. For detection of other microorganisms, a different dopant is to be used. Even the concentration of dopants is very specific for a particular microorganism. The sensitivity (S) of the sensor is defined as: $S = (I_e-I_o)/I_o$, where I_e and I_o are the current values with and without exposure to the microorganism, respectively. The sensitivity of the polyaniline/MPSS sensors upon exposure to *E. coli*, pseudomonas and yeast is shown in Fig. 4. The sensitivity trend shows an initial rise within a few per cent of exposure to microorganism and reaches a saturation value with time. Moreover, for the *E. coli*, a peak value of more than 1000 is reached within about 3–4 s. The sensor sensitivity to pseudomonas and yeast is very low, due to the particular doping combination in the polymer, which makes the sensor specific for a particular species. Since the cell wall of the microorganisms is charged, it can be assumed that the microorganisms carry an electric charge with them. This charge interacts with the polymer thin film rich of dangling bonds. The physical adsorption of microorganisms and their charges affect the surface characteristics of the sensing film. Since the changes in electrical characteristics are reversible, after removal of the microorganisms, it can be assumed that the interaction between sensor and microorganisms is only physical in nature, by exchange of charges between the microorganism and the sensor. Moreover, since there is no physical contact of the microorganism with the sensor, we can state that it is a solid–gas interaction at the PANI–air interface. No chemical reaction occurs at the interface and the sensor returns back to its original state within a few seconds, called the response time. Figure 5 shows the sensor response upon exposure and removal of microorganism for two different sensors, one with polyaniline deposited on a macroporous membrane and the other with the sensing film deposited on flat silicon.

We notice that the sensitivity and response of the microsensors prepared on macroporous silicon substrates are higher in value per area of the substrate and the response time faster than that of the ones prepared on glass or flat silicon substrates. Figures 4 and 5 show the electrical response from a macroporous and a flat silicon substrate, respectively. The different morphology of the polymer thin films deposited on a flat surface and on a porous silicon substrate are evident from SEM micrographs (Fig. 1). It is noticeable that a polyaniline film deposited in porous substrate shows a larger surface area and a higher degree of crystallinity.

The crystallinity of the film deposited on a porous substrate is confirmed by the X-ray pattern reported in Fig. 3. The X-ray diffraction shows an amorphous structure of polyaniline films deposited on flat surface, while the X-ray diffraction pattern of polyaniline films deposited on MPSS clearly shows the crystalline peaks indicating a strong crystallinity degree in the sensing film. The crystallinity and the larger area provided by the macroporosity of the substrate are responsible for the enhanced sensitivity and the faster response time of the polyaniline/MPSS sensors.

4. Conclusion

Integrated microsystems prepared from Fe-doped polyaniline thin film vacuum deposited on macroporous silicon substrates have been found to exhibit excellent sensitivity and fast response for *E. coli*. Behavioural acceptance tests have shown that these sensors are highly specific and selective. The high sensitivity arises from the integration of polymer crystallites at microlevel on porous structure of silicon substrate. The sensitivity of the sensors has been observed to be high and detection limit low. The stability, reproducibility and shelf life are good.

Acknowledgement

References

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